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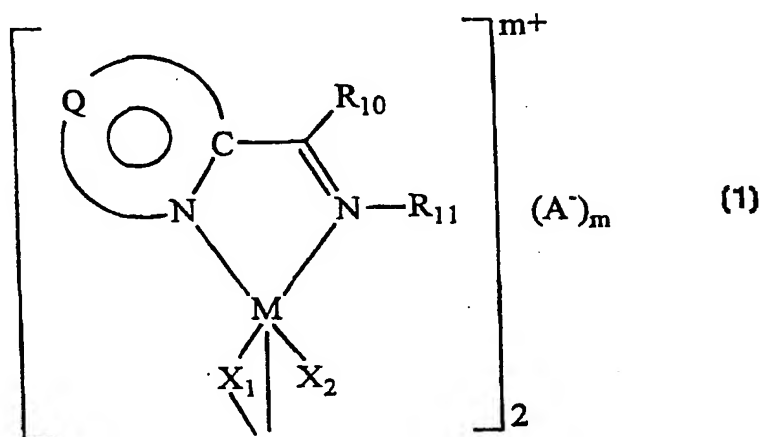
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<p>(21) International Application Number: PCT/FI99/00803 (22) International Filing Date: 29 September 1999 (29.09.99) (30) Priority Data: 982090 29 September 1998 (29.09.98) FI (71) Applicant (for all designated States except US): BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): LAINE, Timo [FI/FI]; Isosaarentie 3 C 47, FIN-00840 Helsinki (FI). LESKELÄ, Markku [FI/FI]; Rauduntie 19 D, FIN-02130 Espoo (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>

(54) Title: DIMERIC DIIMINE TRANSITION METAL COMPLEX AND CATALYSTS



(57) Abstract

The invention relates to a dimeric late transition metal complex having the formula (1) wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-(CR)_nZ_r-$ wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a heteroatom, and a C_1-C_{30} hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from $-N=$, $-NR'$, R' being hydrogen or a C_1-C_{10} hydro-carbyl, $-S-$ and $-O-$, n is 2 or 3 and r is 0 or 1 when n+r is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when n+r is 4; R_{10} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; R_{11} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; M is cobalt or nickel; X_1 and X_2 are independently selected from a monovalent ligand attached to M; A^- is an anion and m is 0, 1 or 2, one of X_1 and X_2 optionally missing in the case m is 1 or 2, and the open lines from M and X_1 are $M-X_1$ and X_1-M bonds, respectively, between the two mers of the dimer.

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DIMERIC DIIMINE TRANSITION METAL COMPLEX AND CATALYSTS

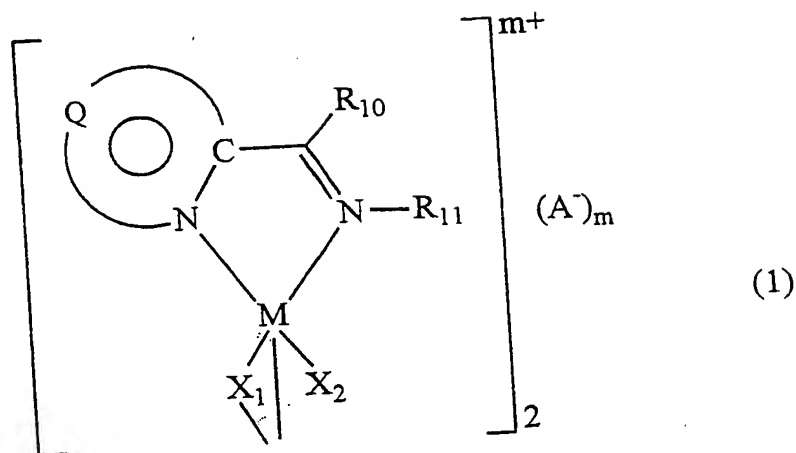
5 The invention relates to a dimeric late transition metal complex. The invention also relates to a late transition metal polymerization catalyst system comprising said complex, and the use of the catalyst system for the polymerization of ethylenically unsaturated compounds.

10 Only recently, see Johnson, L.K., Killian, C.M., Brookhart, M., J. Am. Chem. Soc., 117(1995), 6414, high molecular weight polyethylene was prepared for the first time using late transition metal based catalyst systems. In the PCT-application WO 96/23010, the activation of nickel(II) and palladium(II) complexes bearing sterically demanding 1,4-diazabutadiene ligands by methyl aluminoxane or boron compounds and the polymerization of ethylene by means of the activated complexes were described.

15 In Rülke, R.E., Delis, J.G.P., Groot, A.M., Elsevier, C.J., van Leeuwen, P.W.N.M., Vrieze, K., Goubiz, K., Schenk, H., J. Organometallic Chem., 508(1996)109-120, the preparation of late transition metal complexes comprising different bidentate N-(2-pyridinylmethylene)hydrocarbylamino ligands was described. According to this document, the stability of the complexes were not good. Thus chloromethyl-[N-
20 (2-pyridinylmethylene)-2-phenylethylamine]palladium was only stable for a few hours. As the activation of such complexes with e.g. aluminoxane destabilizes them still further, it was not expected that they could be used as stable polymerization catalyst components.

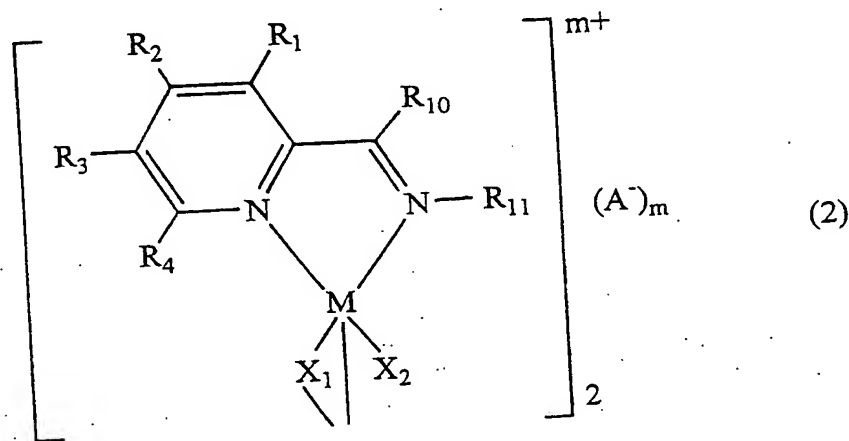
25 In the present invention, it was surprisingly found that certain dimeric late transition metal complexes were, contrary to the teaching of said document by Rülke et al., very stable. Additionally, they were activatable by e.g. aluminoxane and catalytically active in the polymerization of ethylenically unsaturated compounds.

The dimeric late transition metal complexes according to the invention have the following general formula (1)



wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-[(CR)_nZ_r]-$ wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a hetero-atom, and a C_1-C_{30} hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from $-N=$, $-NR'-$, R' being hydrogen or a C_1-C_{10} hydrocarbyl, $-S-$ and $-O-$, n is 2 or 3 and r is 0 or 1 when n+r is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when n+r is 4; R_{10} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; R_{11} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; M is cobalt or nickel; X_1 and X_2 are independently selected from a monovalent ligand attached to M; A^- is an anion and m is 0, 1 or 2, one of X_1 and X_2 optionally missing in the case m is 1 or 2, and the open lines from M and X_1 are $M-X_1$ and X_1-M bonds, respectively, between the two mers of the dimer.

Compared to earlier monomeric late transition metal complexes unexpected improvement and advantage has been achieved with a dimeric complex preferably having the formula (2)



wherein each of R_1 - R_4 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R_{10} is a group selected from hydrogen and a hydrocarbyl containing from 1 to 10 carbon atoms, R_{11} is an aromatic group and M, X_1 , X_2 , A⁻ and m are the same as above.

Thus, it has been realized that dimeric late transition metal complexes comprising a bidentate N-(2-pyridinylmethylene)arylamino ligand are stable, activatable and active as catalysts in the polymerization of ethylenically unsaturated compounds.

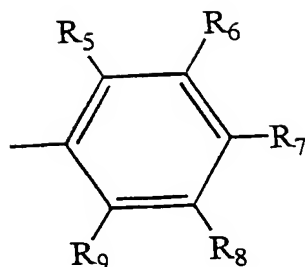
In formula (2), the pyridine ring substituents R_1 - R_4 may be a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group. Typical organic groups are C_1 - C_{10} alkyls, C_6 - C_{18} aryls, C_7 - C_{19} aralkyls and C_7 - C_{19} alkaryl. Typical ring constituents are those in which R_1 and R_2 or R_2 and R_3 form together an aromatic ring which is fused with the pyridine ring to form isoquinoline. Further R_3 and R_4 may form together an aromatic ring which is fused with the pyridine ring to form quinoline. Larger fused ring systems like the three-ring phenanthridine may also be used. Typical inorganic atoms or groups are e.g. nitro, halogen and acyl, provided that they are unreactive towards other moieties of the complex and non-coordinating. This criterion is also valid for the above ring substituents R_1 - R_4 .

Although the pyridine ring may have various non-reactive and non-coordinating substituents, R_1 - R_4 are preferably a hydrogen.

In formula (2), R_{10} is a group selected from a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms. R_{10} must also be internally unreactive and non-coordinating. Preferably, R_{10} is a hydrogen.

In the preferred dimeric late transition metal complex according to the invention and expressed by formula (2), the group R_{11} may be any internally unreactive and non-coordinative aromatic substituent. By aromatic group is meant any group structure having a particularly stable series of occupied π -molecular orbitals. The aromatic group is typically described by the Hückel rule, according to which planar monocyclic completely conjugated hydrocarbons will be aromatic when the ring contains $4n+2$ π -electrons, wherein n is the number of ring carbon atoms. Thus, all annulenes according to the Hückel rule are included. In addition, fused ring systems of aromatic type, as well as homoaromatic (partly aromatic) rings are also suitable.

Preferably, the aromatic group Ar has the formula (3)



(3)

wherein each of R_5 - R_9 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group. Naturally, these substituents are also internally unreactive and non-coordinating.

In formula (3), typical organic groups R_5 - R_9 are C_1 - C_{10} alkyls, C_6 - C_{18} aryls, C_7 - C_{19} aralkyls and C_7 - C_{19} alkaryl. Typical ring constituents R_5 - R_9 form with the disclosed ring fused ring systems like naphthalene, anthracene, phenanthrene, etc., provided that they are non-coordinating and allow the coordination of the nitrogen atoms of the ligand to the late transition metal.

Preferably, R_6 - R_8 are a hydrogen and R_5 and R_9 are independently selected from a C_1 - C_{20} alkyl, a C_6 - C_{24} aryl, a C_7 - C_{30} alkaryl or a C_7 - C_{30} aralkyl. More preferably, R_5 and R_9 are independently a branched C_3 - C_{10} alkyl, such as isopropyl or tert. butyl. Most preferably, R_5 and R_9 are isopropyl.

The late transition metal M of the present complex is a transition metal selected from Groups 8-10 of the Periodic Table of the Elements (IUPAC 1990) which forms said dimeric complex, such as cobalt or nickel. According to the IUPAC recommendation of 1990, the Groups are numbered 1-18, whereby Group 8 is the so called Fe group, Group 9 is the so called Co group and Group 10 is the so called Ni group. M is preferably a transition metal selected from Groups 9 or 10 of said Periodic Table of the Elements, most preferably cobalt or nickel.

In addition to said bidentate ligand, the claimed late transition metal complex of formula (2) has one or two further ligands (or ions), X_1 and X_2 , bonded to the metal M. These ligands may be any monovalent (mono-dentate) ligand capable of forming a coordination bond with the metal M and being unreactive towards the other ligands of the complex. The ligands X_1 and X_2 may be part of a dimer bridge and, optionally, be a cationic or cation inducing species. Typically, halogens form bridges and electron donating compounds such as tetrahydrofurane THF form

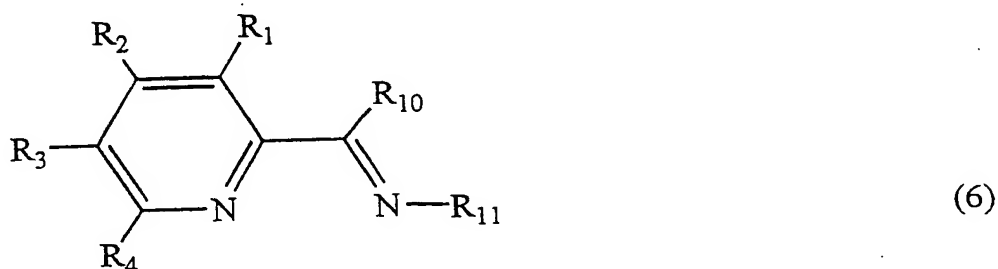
cations. In the case of cations, the other of X_1 and X_2 , preferably a halogen, may optionally be missing.

Preferably, the monovalent ligands X_1 and X_2 are independently a hydrogen, a halogen, a C_1 - C_{12} hydrocarbyl, a C_1 - C_{12} hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound. Most preferably, X_1 and X_2 are independently a halogen, preferably chlorine or bromine, or a C_1 - C_5 alkyl, preferably methyl. As halogens form the strongest bridges, the mers of the dimer preferably have at least one halogen as the ligand X_1 or X_2 .

Although the invention also relates to said complex in the form of an ion pair, A^- being e.g. the strong anion $[B(C_6F_5)_4]^-$, the complex is preferably neutral, that is, in formula (2), m is preferably 0.

Typically, the present late transition metal complex is selected from di- μ -chlorodichlorobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis[2,6-dimethyl-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis{2,6-bis(1-methylethyl)-N-[(6-methyl-2-pyridinyl)methylene]phenylamine}dinickel(II), di- μ -bromodibromobis{2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) and di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(phenyl-2-pyridinylmethylene)phenylamine]dinickel(II).

The invention also relates to a process for the preparation of the late transition metal complex described above. For example, in the process, an N-(2-pyridinylmethylene)arylamine of the formula (6)



wherein each of R_1 - R_4 is a non-coordinating substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R_{10} is a non-coordinating group selected from a hydrogen or an organic group containing from 1 to 10 carbon atoms,

and R_{11} is a non-coordinating aromatic group, is reacted with a compound of the formula (7)



(7a)

or



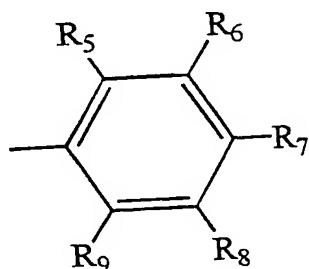
(7b)

5

10

wherein D is an exchangeable bidentate ligand, M is a transition metal selected from one of Groups 8-10 of the Periodic Table of the Elements (IUPAC 1990), and X_1 and X_2 are independently a monovalent ligand, the reaction product is recovered, and, optionally, in the case m is 1 or 2, said reaction product is further reacted with an ion exchanging compound comprising a cation and a non-coordinating anion A^- .

With respect to R_1 - R_4 in formula (6), they are as defined above in connection with formula (2), i.e. preferably a hydrogen. The same applies for R_{10} and R_{11} , whereby in formula (6), Ar preferably has the formula (3)

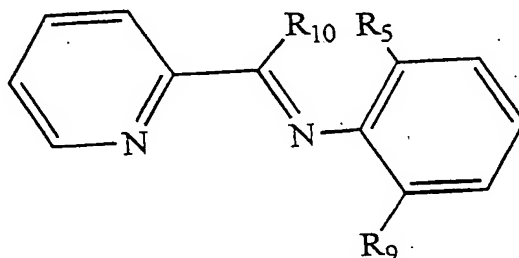


(3)

15 wherein each of R_5 - R_9 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms or an inorganic atom or group.

Most preferably, said N-(2-pyridinylmethylene)arylamine of formula (6) has the specific formula (8)

20



(8)

wherein R_{10} is the same as above, R_5 and R_9 are independently a C_1 - C_{20} alkyl, a C_6 - C_{24} aryl, a C_7 - C_{30} alkaryl or a C_7 - C_{30} aralkyl.

- 5 In accordance with the corresponding substituents of the claimed late transition metal complex, R_{10} is preferably a hydrogen and R_5 and R_9 are preferably independently a branched C_3 - C_{10} alkyl, more preferably isopropyl or tert. butyl, most preferably isopropyl.

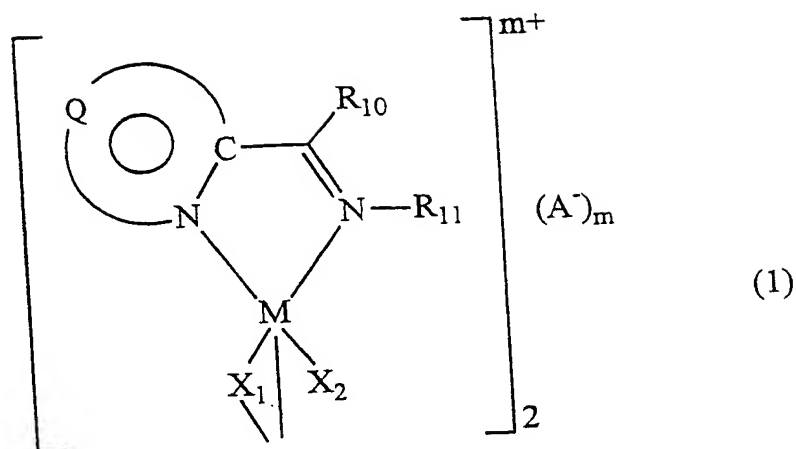
A typical N-(2-pyridinylmethylene)arylamine useful in the preparation of the described late transition metal complex is 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine.

- 10 According to the claimed complex preparation process, the N-(2-pyridinylmethylene)arylamine is reacted with a compound of the above formula (7a) having an exchangeable bidentate ligand, or, in the case of some late transition metals, directly with a compound of the above formula (7b) having only the two stationary ligands X_1 and X_2 bound to the metal. The former is often the case with Ni and the
15 latter is often the case e.g. with Co.

When using exchangeable bidentate ligands, they are preferably bidentate dienes or bidentate diethers, which are capable of coordinating with the late transition metal. Preferably, in formula (7a), the exchangeable bidentate ligand D is selected from 1,5-cyclooctadiene and 1,2-dimethoxyethane.

- 20 As the late transition metal of formula (7) will remain in the final complex, the same applies for it as is stated above in connection with the complex of the invention. Thus, M is preferably a transition metal selected from Groups 9 or 10 of the Periodic Table of the elements (IUPAC 1990), most preferably cobalt or nickel. The same applies for X_1 and X_2 , i.e. in formula (7), X_1 and X_2 are preferably
25 independently a hydrogen, a halogen, a C_1 - C_{12} hydrocarbyl, a C_1 - C_{12} hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound. Most preferably, X_1 and X_2 are independently a halogen, preferably chlorine or bromine, or a C_1 - C_5 alkyl, preferably methyl.

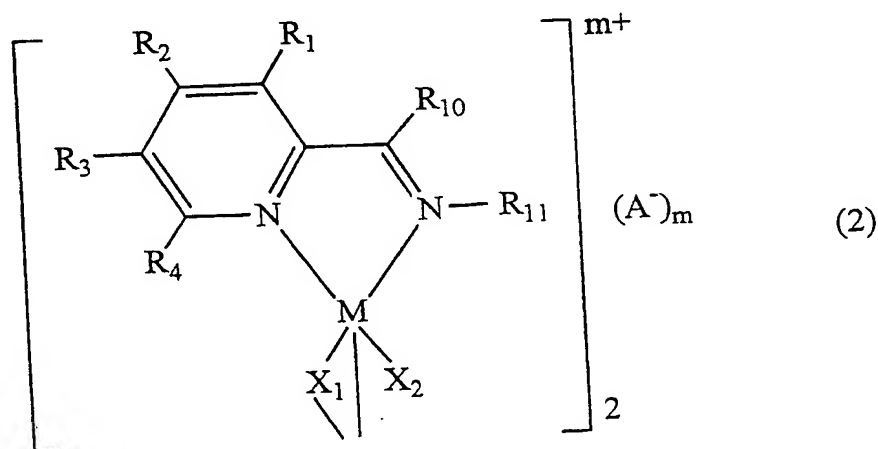
- 30 The invention also relates to a late transition metal catalyst system for the polymerization of ethylenically unsaturated compounds. It comprises a dimeric late transition metal complex having the formula (1)



- wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-[(CR)_nZ_r]-$ wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a hetero-atom, and a C_1-C_{30} hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from $-N=$, $-NR'-$, R' being hydrogen or a C_1-C_{10} hydrocarbyl, $-S-$ and $-O-$, n is 2 or 3 and r is 0 or 1 when $n+r$ is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when $n+r$ is 4; R_{10} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; R_{11} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; M is cobalt or nickel; X_1 and X_2 are independently selected from a monovalent ligand attached to M; A^- is an anion and m is 0, 1 or 2, one of X_1 and X_2 optionally missing in the case m is 1 or 2, and the open lines from M and X_1 are M- X_1 and X_1 -M bonds, respectively, between the two mers of the dimer.

The late transition metal catalyst system preferably comprises:

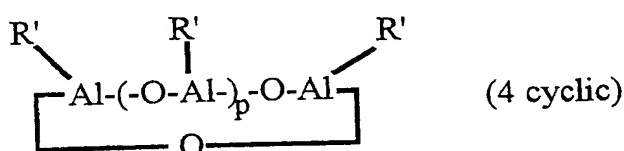
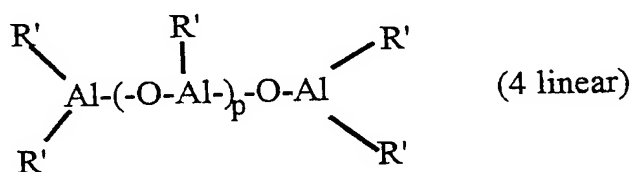
- a) a dimeric late transition metal complex component having the formula (2)



wherein each of R_1 - R_4 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R_{10} is a group selected from hydrogen and a hydrocarbyl containing from 1 to 10 carbon atoms, R_{11} is an aromatic group and M, X_1 , X_2 , A⁻ and m are the same as above, and

b) a cocatalyst component selected from

(i) an aluminoxane having one of the following formulas (4)



wherein each R' is the same or different and is a C_1 - C_{10} alkyl group and p is an integer between 1 and 40, and

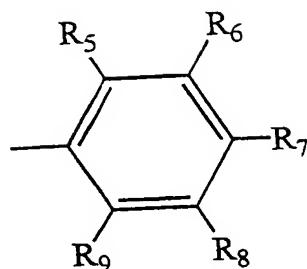
(ii) an organometallic compound having the formula (5)



wherein R'' is a C_1 - C_{10} hydrocarbyl, X' is a halogen, q is 1, 2 or 3, r is the valency of M, M is a metal selected from Groups 1 to 3 and 13 of the Periodic Table of the Elements (IUPAC 1990), and s is 1 or 2.

If said organometallic compound having the formula (5) is used, M is preferably Al.

With respect to the dimeric late transition metal component defined in paragraph a) above the definition is the same as for the dimeric late transition metal complex defined before. Thus, R_1 - R_4 are preferably a hydrogen. Preferably R_{11} has the formula (3)



(3)

wherein each of R_5 - R_9 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group. R_6 - R_8 are preferably a hydrogen, R_5 and R_9 are preferably independently selected from a C_1 - C_{20} alkyl, a C_6 - C_{24} aryl, a C_7 - C_{30} alkaryl or a C_7 - C_{30} aralkyl.

Most preferably R_{10} is a hydrogen and R_5 and R_9 are independently a branched C_3 - C_{10} alkyl such as isopropyl or tert. butyl. M is preferably a transition metal selected from Groups 9 or 10 of the Periodic Table of the Elements (IUPAC 1990) which forms a dimer of the above type, such as cobalt or nickel. X_1 and X_2 are e.g. independently a hydrogen, a halogen, a C_1 - C_{12} hydrocarbonyl, a C_1 - C_{12} hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound. Preferably, X_1 and X_2 are independently a halogen, preferably chlorine or bromine, or a C_1 - C_5 alkyl, preferably methyl. m is usually 0.

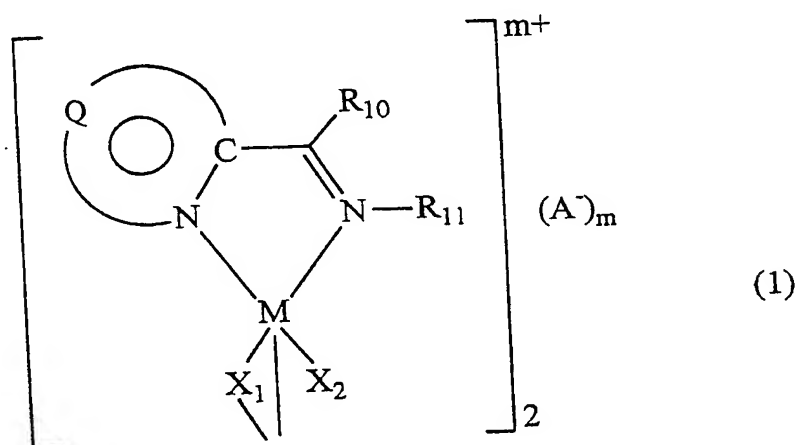
Said late transition metal complex component is according to one embodiment of the invention selected from di- μ -chlorodichlorobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis[2,6-dimethyl-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di- μ -bromodibromobis{2,6-bis(1-methylethyl)-N-[(6-methyl-2-pyridinyl)methylene]-phenylamine}dinickel(II), di- μ -bromodibromobis{2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) and di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(phenyl-2-pyridinylmethylene)phenylamine]dinickel(II).

In its widest scope, the cocatalyst or activator is selected from aluminoxanes of formula (4) and the alkyl metal halides or alkyl metal compounds of formula (5). The alkyl metal halides or alkyl metal compounds such as trimethyl aluminium, triethyl aluminium and triisobutyl aluminium are generally used when the system is supported e.g. on an inorganic oxide such as silica, alumina, silica-alumina, $MgCl_2$, etc. Aluminoxanes are generally used in homogenous systems when the catalyst

system is in solution. Preferably said cocatalyst component is a C₁-C₁₀ alumin-oxane, most preferably methyl aluminoxane.

In order to give as good polymerization results as possible when polymerizing ethylenically unsaturated compounds, the molar ratio Al/M is preferably between 10 and 10000, most preferably between 500 and 5000.

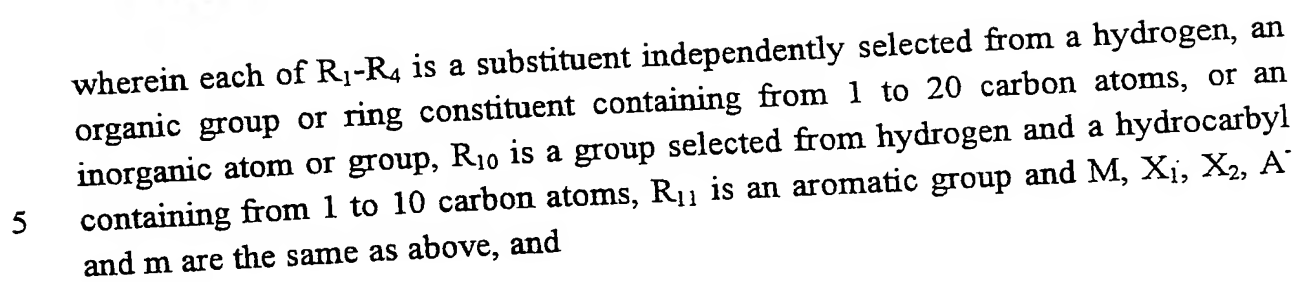
Last but not least, the invention relates to process for the polymerization of ethylenically unsaturated compounds. In the claimed polymerization process, under polymerization conditions, at least one polymerizable ethylenically unsaturated compound is contacted with a catalyst system comprising a dimeric late transition metal complex having the formula (1)



wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula -[(CR)_nZ_r]- wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a hetero-atom, and a C₁-C₃₀ hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from -N=, -NR'-, R' being hydrogen or a C₁-C₁₀ hydrocarbyl, -S- and -O-, n is 2 or 3 and r is 0 or 1 when n+r is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when n+r is 4; R₁₀ is hydrogen, a halogen or a C₁-C₃₀ hydrocarbyl; R₁₁ is hydrogen, a halogen or a C₁-C₃₀ hydrocarbyl; M is cobalt or nickel; X₁ and X₂ are independently selected from a monovalent ligand attached to M; A⁻ is an anion and m is 0, 1 or 2, one of X₁ and X₂ optionally missing in the case m is 1 or 2, and the open lines from M and X₁ are M-X₁ and X₁-M bonds, respectively, between the two mers of the dimer.

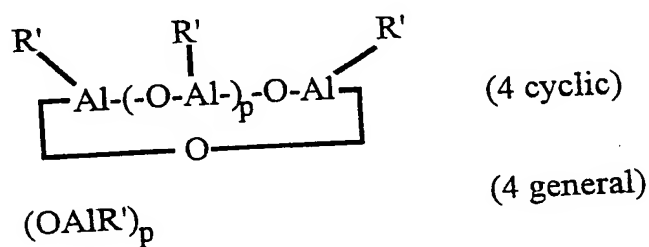
Preferably, the catalyst system comprises

a) a late transition metal complex component having the formula (2)



b) a cocatalyst component selected from

(i) an aluminoxane having one of the following formulas (4)



10 wherein each R' is the same or different and is a C₁-C₁₀ alkyl group and p is an integer, between 1 and 40, and

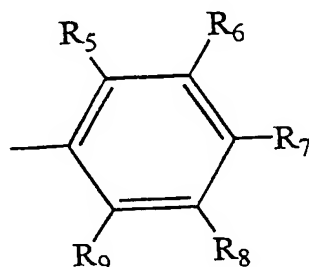
(ii) an organometallic compound having the formula (5)



(5)

wherein R" is a C₁-C₁₀ hydrocarbyl, X' is a halogen, q is 1, 2 or 3, r is the valency of M, M is a metal selected from Groups 1 to 3 and 13 of the Periodic Table of the Elements (IUPAC 1990), and s is 1 or 2.

For the catalyst system used in the claimed polymerization process, the same applies as for the description above concerning the catalyst system as a product. Thus, in
 5 formula (2), R₁-R₄ are preferably a hydrogen. Preferably Ar has the formula (3)



(3)

wherein each of R₅-R₉ is a substituent independently selected from a hydrogen, an
 10 organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group. R₆-R₈ are preferably a hydrogen, R₅ and R₉ are preferably independently selected from a C₁-C₂₀ alkyl, a C₆-C₂₄ aryl, a C₇-C₃₀ alkaryl or a C₇-C₃₀ aralkyl. Most preferably R₁₀ is a hydrogen (see formula (2)) and R₅ and R₉ are independently a branched C₃-C₁₀ alkyl such as isopropyl or tert. butyl.

In formula (1 and 2), M is preferably a transition metal selected from Groups 9 or
 15 10 of the Periodic Table of the Elements (IUPAC 1990), such as cobalt or nickel. X₁ and X₂ are e.g. independently a hydrogen, a halogen, a C₁-C₁₂ hydrocarbyl, a C₁-C₁₂ hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound. Preferably, X₁ and X₂ are independently a halogen, preferably chlorine or bromine, or a C₁-C₅ alkyl, preferably methyl. m is usually 0.

20 Said late transition metal complex component is in the polymerization process preferably selected from di-μ-chlorodichlorobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di-μ-bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di-μ-bromodibromobis[2,6-dimethyl-N-(2-pyridinylmethylene)phenylamine]dinickel(II), di-μ-bromodibromobis{2,6-bis(1-methylethyl)-N-[(6-methyl-2-pyridinyl)methylene]-
 25 phenylamine}dinickel(II), di-μ-bromodibromobis{2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) and di-μ-bromodibromobis[2,6-bis(1-methylethyl)-N-(phenyl-2-pyridinylmethylene)phenylamine]dinickel(II).

In said polymerization process, said cocatalyst component is preferably a C₁-C₁₀ aluminoxane, most preferably methyl aluminoxane. The molar ratio Al/M is preferably between 10 and 10000, most preferably between 500 and 5000.

- 5 The claimed polymerization process is suitable for a number of ethylenically unsaturated compounds as monomers. It is e.g. suitable for the polymerization of olefins such as ethylene, propylene, 1-butene, 1-hexene, cyclopentene, cyclobutene and norbornene. It is also suitable e.g. for the copolymerization of ethylene/-propylene, ethylene/1-butene, ethylene/1-hexene, ethylene/1,3-butadiene, ethylene/-4-methyl-1-pentene, ethylene/ α - ω -diolefins such as α - ω -octadiene, propylene/-cyclopentene, ethylene/norbornene, ethylene/dimethanooctahydrohaphthalene and ethylene/propylene/ethylidene norbornene. Preferably, said polymerizable ethylenically unsaturated compound is selected from ethylene, an α -C₃-C₂₀-olefin and a conjugated polymerizable ethylenically unsaturated compound. Most preferably, the polymerizable ethylenically unsaturated compound is ethylene or a mixture thereof with an α -C₃-C₁₀-olefin.
- 10
- 15

Examples

Figure Captions

Fig. 1 Crystal structure of complex 1 showing labeling scheme.

- Fig. 2 Crystal structure of complex 2 showing the labeling scheme. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni-N1 2.039(2), Ni-N8 2.095(2), Ni-Cl1 2.3965(8), Ni-Cl1a 2.3366(8), Ni-Cl2 2.2729(9), C6-C7 1.463(4), C7-N8 1.278(3), N8-C9 1.440(3); N1-Ni-N8 79.37(9), N1-Ni-Cl1 91.08(6), N1-Ni-Cl1a 161.14(6), N1-Ni-Cl2 94.00(6), Cl1-Ni-Cl1a 85.53(3), Ni-Cl1-Nia 94.47(3).
- 20

- Fig. 3 Crystal structure of complex 3 with the labeling scheme. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.
- 25

Fig. 4 Molecular structure of compound 4 showing the two crystallographically independent molecules of the asymmetric unit.

- Fig. 5 Crystal structure of complex 5.
- 30

Fig. 6 Molecular structure of compound 6. The solvent molecules are omitted for clarity.

Examples 1 and 2

A. Preparation of the complexes

General

- All complex preparations were performed under argon atmosphere using standard
5 Schlenk techniques. Acetone was dried by storing under argon with CaSO₄ granules,
other solvents by refluxing with a drying agent (P₂O₅ for dichloromethane and
sodium/benzophenone for the non-halogenated solvents) and distillation under
argon. Dichloro(1,2-dimethoxyethane)nickel(II), (DME)NiCl₂, and dibromo(1,2-di-
methoxyethane)nickel(II), (DME)NiBr₂, were prepared according to the literature.
10 2-pyridinecarboxaldehyde (Merck, 98 %), and 2,6-di(1-methylethyl)phenylamine
(Aldrich, 90 %) were used as received. ¹H NMR: Varian Gemini 200 spectrometer
(200 MHz); CDCl₃, or [D₆]acetone as solvent, TMS as internal standard. Elemental
analyses were carried out at the University of Ulm, Germany.

2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine (L₁)

- 15 The ligand was synthesized by modifying the literature method reported for the
analogous 2,6-dimethyl compound. Ethanol (100 ml), 2,6-di(1-methylethyl)phenyl-
amine (15.76 g, 80.0 mmol), and 2-pyridinecarboxaldehyde (8.57 g, 80.0 mmol)
were combined and refluxed for 20 min. The solvent was removed and the residue
was vacuum distilled followed by chromatography on basic alumina with pentane/-
20 ethyl acetate (3:1) as eluent. Recrystallization from pentane yielded pale yellow
crystals, 14.36 g (67 %). ¹H NMR (CDCl₃): δ = 1.17 (d, 12H, H_{Me}), 2.97 (m, 2H,
CHMe₂), 7.16 (m, 3H, H_{arom}), 7.42 (m, 1H, H_{pyridine,4}), 7.86 (t, 1H, H_{phenyl,4}), 8.27 (d,
1H, H_{pyridine,3}), 8.31 (s, 1H, CH=N), 8.73 (d, 1H, H_{pyridine,6}). - C₁₈H₂₂N₂ (266.39):
calcd. C 81.16, H 8.32, N 10.52; found C 81.01, H 8.37, N 10.39.

- 25 *Di-μ-chlorodichlorobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenyl-
amine]dinickel(II) (1)*

- To a suspension of (DME)NiCl₂ (1.86 g, 8.45 mmol) in 40 ml dichloromethane was
added the yellow ligand solution (2.34 g, 8.77 mmol in 15 ml CH₂Cl₂). After
stirring the brown reaction mixture for 24 h at room temperature, the solvent was
30 evaporated and the resulting solid material was washed with pentane (3 x 20 ml)
and dried in vacuum yielding complex 2a as orange powder, 2.65 g (79 %).
- C₃₆H₄₄Cl₄N₄Ni₂ (791.97): calcd. C 54.60, H 5.60, N 7.07; found C 54.61, H 5.94,
N 6.68.

Di-μ-bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenyl-amine]dinickel(II) (2)

Analogously to the preparation of 2a, complex 2b was prepared from (DME)NiBr₂ (0.40 g, 1.30 mmol) and L (0.36 g, 4.89 mmol) in CH₂Cl₂. The orange-red powder
5 was collected by filtration, washed with pentane (3 x 10 ml) and vacuum dried; yield 0.44 g (70 %). - C₃₆H₄₄Br₄N₄Ni₂ (969.77): calcd. C 44.59, H 4.57, N 5.78; found C 44.10, H 4.59, N 5.68.

B. Analysis of the complexes

X-ray crystal structure determinations

10 The crystals were mounted to a glass fiber using the oil drop method. Crystal data obtained with the ω-2θ scan mode were collected on an automated four-circle Rigaku AFC-7S diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at 193 K. Three standard reflections were monitored after every
15 200 intensity scans. The intensities were corrected for Lorentz and polarization effects. Data sets were compressed to reflection files with TEXSAN Single Crystal Structure Analysis Software. The structures were solved with SHELXTL PC 4.1 program package using direct methods while further refinement with full-matrix least-squares on F² was carried out with SHELXL 93. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced to calculated positions
20 (riding model) with 1.2 times the displacement factors of the host carbon atoms.

Fig. 1 shows compound 1 and Fig. 2 shows compound 2.

Table 1

Crystallographic data for complex 2

	2
Empirical formula	C ₃₆ H ₄₄ Br ₄ N ₄ Ni ₂
Formula weight	969.81
Crystal color and form	Brown, prismatic
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	9.885(6)
b (Å)	14.515(7)
c (Å)	14.127(7)
α (°)	90
β (°)	106.82(4)
γ (°)	90
V (Å ³)	1940.2(18)
Z	2
D _c (Mg/m ³)	1.660
Absorption coefficient μ (mm ⁻¹)	5.119
F(000)	968
Crystal size (mm)	0.15 x 0.15 x 0.10
Scan mode	ω-2θ
θ _{max} (°)	25.00
Number of collected reflections	3020
Number of independent reflections	2866
Number of parameters	212
Goodness-of-fit on F ²	1.036
Final R indices [I > 2σ(I)]	R=0.0860, wR=0.1894
R indices (all data)	R=0.1374, wR=0.2193
Largest differential peak and hole e/Å ³	1.056 and -1.060

C. Polymerization of complexes 1 and 2

- 5 The polymerization conditions and results with catalysts 1 and 2/MAO are summarized in Table 2. Treatment of nickel complexes 1 and 2 with MAO produces active catalysts for the polymerization of alkenes. In the nickel catalyzed reactions

both the activities and product molecular weights are dependent on the polymerization temperature. As polymerization at 20 °C provides low-melting or waxy polymers with activity comparable to other new systems lowering the temperature to 0 °C leads to an increase in molecular weights by an order of magnitude at the expense of declining catalytic activity. No significant difference in polymer properties was observed between the dichloro and dibromonickel(II) based systems (1/MAO and 2/MAO, respectively), which indicates a similar activation mechanism for both catalysts.

Even though numerous catalyst systems have been developed to date, fine-tuning of the catalyst precursor, and the ligand environment of the precursor in particular, is still one of the major tools to tailor polymer properties.

Table 2

Ethylene polymerization with catalysts 1 and 2/MAO^a

Entry	Catalyst	T _p (°C)	P _{ethylene} (bar)	n _{cat} (μmol)	Yield (g)	Activity ^b	M _w (g mol ⁻¹)
1	1	20	4.3	2.5	3.3	5300	6600
2	1	0	3.0	5.0	1.6	660	45000
3	2	20	4.3	2.5	4.2	6700	4800
4	2	0	3.0	5.0	1.6	620	40000

^aPolymerization conditions: T_p = 15 min (except at 0 °C 30 min), [A1]:[M] = 2000, polymerization medium = toluene. ^bActivity in kg polymer (mol catalyst x h)⁻¹.

Examples 3-6

A. General

All complex preparations were performed under an argon atmosphere using standard Schlenk techniques. Acetone was dried by storing under argon with CaSO₄ granules, other solvents by refluxing with a drying agent (CaH₂ for dichloromethane and sodium/benzophenone for the nonhalogenated solvents) and distillation under argon. Commercial reagents, namely 1-(2-pyridinyl)ethanone (Merck, 98%), phenyl-2-pyridinylmethanone (Merck, 98%), and 2,6-di(1-methylethyl)phenylamine (Aldrich, 90%), were used as received. Dibromo(1,2-dimethoxyethane)nickel(II) [(DME)NiBr₂] [29], 2,6-dimethyl-N-(2-pyridinylmethylene)phenylamine (L₂) [21] and 2,6-bis(1-methylethyl)-N-[(6-methyl-2-pyridinyl)methylene]phenylamine (L₃)

[22] were prepared as reported earlier. Synthesis products were characterized, when applicable, using a Varian Gemini 200 spectrometer (200 MHz) with CDCl_3 as solvent and TMS as internal standard. Elemental analyses were carried out at the University of Ulm, Germany.

- 5 Polymerization procedure and equipment have been described in detail above. For polymer molecular weights and molecular weight distributions a Waters 150-C GPC chromatograph was used operating at 135 °C with 1,2,4-trichlorobenzene solvent and polystyrene calibration standards. Melting temperatures of preheated and cooled samples were determined by differential scanning calorimetry using a Perkin Elmer
- 10 DSC-2 calorimeter. Analysis of polymer microstructure was based on NMR spectra recorded on a Varian XL-300 spectrometer at 125 °C. Samples were dissolved in 1,1,2,2-tetrachloroethane- d_2 and a 10:1 weight ratio mixture of 1,2,4-trichlorobenzene and benzene- d_6 for ^1H and ^{13}C NMR measurements, respectively.

B. Ligand and complex preparation

- 15 *2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene]phenylamine (L₄)*

The ketone 1-(2-pyridinyl)ethanone (1.82 g, 15.0 mmol) was combined with 2,6-di(1-methylethyl)phenylamine (3.57 g, 18.1 mmol) and three drops of concentrated sulfuric acid as well as some sodium sulfate was added. This mixture was heated to 120 °C and stirring was continued at this temperature for 24 h. The dark brown, oily

- 20 raw product was dissolved in 50 ml of dichloromethane, filtered, washed with 50 ml of water and dried with Na_2SO_4 . After filtration and solvent evaporation the yellow-brown residue was purified by crystallization from ethanol affording yellow, cubic crystals; yield 1.41 g (34%). $\text{C}_{19}\text{H}_{24}\text{N}_2$ (280.41) Anal. calc.: C 81.38; H 8.63; N 9.99%. Found: C 81.36; H 8.65; N 10.21%. ^1H NMR (CDCl_3): δ 1.15 (d, 12H, H_{Me}), 2.21 (s, 3H, $\text{H}_{\text{bridge-Me}}$), 2.75 (m, 2H, CHMe_2), 7.11-7.20 (m, 3H, H_{phenyl}), 7.39 (m, 1H, $\text{H}_{\text{pyridine,5}}$), 7.82 (t, 1H, $\text{H}_{\text{pyridine,4}}$), 8.36 (d, 1H, $\text{H}_{\text{pyridine,3}}$), 8.69 (d, 1H, $\text{H}_{\text{pyridine,6}}$) ppm.

2,6-bis(1-methylethyl)-N-(phenyl-2-pyridinylmethylene)phenylamine (L₅)

- 30 Analogously to the preparation of L_4 , compound L_5 was synthesized from phenyl-2-pyridinylmethanone (2.75 g, 15.0 mmol) and 2,6-di(1-methylethyl)phenylamine (3.29 g, 16.7 mmol) at 120 °C. The ligand was obtained from ethanol as bright yellow microcrystalline powder, 1.68 g (33%). $\text{C}_{24}\text{H}_{26}\text{N}_2$ (342.48) Anal. calc.: C 84.17; H 7.65; N 8.18%. Found: C 84.04; H 7.72; N 8.37%. ^1H NMR (CDCl_3): δ 0.90 (d, 3H, H_{Me}), 0.97 (d, 3H, H_{Me}), 1.14 (d, 6H, H_{Me}), 2.93 (m, 2H, CHMe_2),

6.98-7.23 (m, 6H, H_{arom}), 7.45 (m, H_{arom}), 7.83 (m, H_{arom}), 8.25 (d, H_{arom}), 8.64 (m, H_{arom}) ppm.

Di-μ-bromodibromobis[2,6-dimethyl-N-(2-pyridinylmethylene)phenylamine]-dinickel(II) (3)

- 5 To a suspension of [(DME)NiBr₂] (2.03 g, 6.6 mmol) in 20 ml of CH₂Cl₂ was added the solution of ligand L₂ (1.42 g, 6.8 mmol) in 20 ml of CH₂Cl₂. The orange-red reaction mixture was stirred for 24 h at room temperature, after which the precipitate was collected by filtration, washed with pentane (2x10 ml), and vacuum-dried yielding complex 3 as orange-yellow powder, 1.55 g (55%). C₂₈H₂₈Br₄N₄Ni₂ (857.55) Anal. calc.: C 39.22; H 3.29; N 6.53%. Found C 38.97; H 3.60; N 6.39%.
- 10

Compounds 4-6 were prepared analogously from [(DME)NiBr₂] and the corresponding ligand in dichloromethane.

Di-μ-bromodibromobis{2,6-bis(1-methylethyl)-N-[(6-methyl-2-pyridinyl)-methylene]phenylamine}dinickel(II) (4)

- 15 Orange-yellow powder, yield 57%. C₃₈H₂₈Br₄N₄Ni₂ (997.82) Anal. calc.: C 45.74; H 4.85; N 5.61%. Found: C 45.56; H 4.81; N 5.53%.

Di-μ-bromodibromobis{2,6-bis(1-methylethyl)-N-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (5)

- Bright orange powder, yield 62%. C₃₈H₂₈Br₄N₄Ni₂ (997.82) Anal. calc.: C 45.74; H 4.85; N 5.61%. Found: C 45.44; H 4.84; N 5.69%.
- 20

Di-μ-bromodibromobis[2,6-bis(1-methylethyl)-N-(phenyl-2-pyridinylmethylene)-phenylamine]dinickel(II) (6)

Orange-brown powder, yield 77%. C₄₈H₅₂Br₄N₄Ni₂ · CH₂Cl₂ (1206.89) Anal. calc.: C 48.76; H 4.51; N 4.64%. Found: C 48.44; H 5.05; N 4.55%.

25 C. X-ray crystallography

- The crystals were mounted to a glass fiber using the oil drop method [30]. Crystal data obtained with the ω2θ scan mode were collected on an automated four-circle Rigaku AFC-7S diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 193 K (except for complex 7 at 213 K). Three standard reflections were monitored after every 200 intensity scans. The intensities were
- 30

corrected for Lorentz and polarization effects. For all compounds ψ -scans were used for absorption correction [31]. Data sets were compressed to reflection files with TEXSAN Single Crystal Structure Analysis Software [32]. Structure solution using direct methods and further refinement with full-matrix least-squares on F^2 was carried out with SHELX97 [33]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced to calculated positions (riding model) with 1.2 times the displacement factors of the host carbon atoms. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 133658 (for 3), 133659 (for 4), 133660 (for 5) and 133661 (for 6). Copies of this information can be obtained free of charge from: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336 033; E-mail: deposit@ccdc.cam.ac.uk.

Table 3 Ethylene polymerization with catalysts 3-6/MAO.^a

Entry	Catalyst	T _p ^b (°C)	n _{cat} (μmol) ^c	p (bar) ^d	Yield (g)	Activity ^e	M _w (g mol ⁻¹)	M _w /M _n	T _m (°C) ^f	Methyls per 1000 carbon atoms ^g
1	3	40	2.5	5.5	4.44	3600	2800	1.7	wax	43
2	3	20	2.5	4.3	7.08	5700	5500	2.2	113.3 ^h	24
3	3	0	5.0	3.0	3.07	610	26000	1.9	127.0	6
4	4	40	5.0	5.5	1.20	480	5600	2.2	116.7 ^h	28
5	4	20	10	4.3	2.93	590	7900	2.7	118.0 ^h	23
6	4	0	20	3.0	0.86	43	27000	2.0	127.0	7
7	5	40	2.5	5.5	3.80	3000	3400	1.8	wax	83
8	5	20	5.0	4.3	12.16	4800	5000	2.6	101.7 ^h	50
9	5	0	5.0	3.0	3.02	600	22000	2.4	116.3	17
10	6	40	4.6	5.5	7.12	3100	2300	2.5	wax	67
11	6	20	4.6	4.3	2.28	990	7000	2.1	101.3 ^h	53
12	6	0	4.6	3.0	4.64	1000	30000	2.9	115.7	24

^a [Al]:[M] = 2000, T_p = 30 min (except at 0 °C 60 min). ^b Polymerization temperature. ^c Molar amount of the catalyst precursor (in μmol Ni). ^d Ethylene pressure. ^e Activity in kg PE (mol catalyst x h)⁻¹. ^f Peak melting temperature. ^g Determined by ¹H NMR spectroscopy. ^h Broad melting peak.

Table 4 Crystallographic data for complexes 3-6

	3	4	5	6
Empirical formula	$C_{28}H_{28}Br_4N_4Ni_2$	$C_{38}H_{48}Br_4N_4Ni_2$	$C_{38}H_{48}Br_4N_4Ni_2$	$C_{48}H_{52}Br_4N_4Ni_2 \cdot 4CH_2Cl_2$
Formula weight	857.55	997.82	997.82	1461.69
Crystal color and form	Orange, prismatic	Red, prismatic	Red, prismatic	Red, prismatic
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal system	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Space group				
a (Å)	12.118(7)	10.319(4)	14.311(4)	11.971(4)
b (Å)	10.425(3)	19.802(4)	10.240(4)	14.369(3)
c (Å)	12.438(7)	20.691(6)	14.335(5)	18.180(4)
β (°)	102.75(4)	93.84(3)	110.95(2)	107.04(2)
V (Å ³)	1532.5(13)	4218(2)	1961.8(12)	2989.9(13)
Z	2	4	2	2
D _c (Mg/m ³)	1.858	1.571	1.689	1.624
Absorption coefficient μ (mm ⁻¹)	6.467	4.711	5.065	3.698
F(000)	840	2000	1000	1464
Crystal size (mm)	0.23x0.11x0.10	0.48x0.40x0.35	0.30x0.25x0.22	0.30x0.26x0.24
Scan mode	$\omega 2\theta$	$\omega 2\theta$	$\omega 2\theta$	$\omega 2\theta$
Scan mode	26.49	25.00	25.01	25.00
θ_{max} (°)	25.69	6833	3101	4784
Number of unique reflections				

Table 4 Cont.

	3	4	5	6
Empirical formula	$C_{28}H_{28}Br_4N_4Ni_2$	$C_{38}H_{48}Br_4N_4Ni_2$	$C_{38}H_{48}Br_4N_4Ni_2$	$C_{48}H_{52}Br_4N_4Ni_2 \cdot 4CH_2Cl_2$
Number of observed reflections	2011	5625	2512	3952
$[I > 2\sigma(I)]$				
Number of parameters	172	433	222	316
Goodness-of-fit on F^2 ^a	1.030	1.033	1.027	1.021
Final R indices $[I > 2\sigma(I)]$ ^b	R=0.0485, wR=0.0909	R=0.0387, wR=0.0793	R=0.0479, wR=0.1060	R=0.0441, wR=0.0981
R indices (all data) ^b	R=0.0713, wR=0.0980	R=0.0546, wR=0.0839	R=0.0656, wR=0.1130	R=0.0585, wR=0.1031
Largest differential peak and hole ($e/\text{\AA}^3$)	0.526 and -0.664	0.440 and -0.386	0.625 and -0.572	0.591 and -1.127 ^c

^a $S = [\Sigma[w(F_o^2 - F_c^2)] / (n-p)]^{1/2}$ where n = data and p = parameters.

^b $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ with $F > 4\Sigma(F)$; function minimized is $wR = [\Sigma[w(F_o^2 - F_c^2)] / \Sigma[w(F_o^2)]]^{1/2}$.

^c Minimum residual electron density - 1.127 $e/\text{\AA}^3$; hole coordinates x = 0.4818, y = 0.9406, z = 0.1179; distance to nearest atom (Br1) 0.92 \AA .

Table 5 Selected bond lengths (Å) and angles (°) for 3, 4, 5 and 6

3	4	5	6	
Bond lengths				
Ni-N1	2.069(5)	Ni1-N1 Ni2-N22	2.086(3) 2.072(3)	Ni-N1 2.023(5)
Ni-N8	2.042(5)	Ni-N8 Ni2-N29	2.042(3) 2.036(3)	Ni-N8 2.060(5)
Ni-Br1	2.4759(17)	Ni1-Br1 Ni2-Br3	2.5411(12) 2.5230(12)	Ni-Br1 2.5920(12)
Ni-Br1 [#]	2.5479(12)	Ni1-Br1 [*] Ni2-Br3a [§]	2.4806(9) 2.4876(8)	Ni-Br1a [†] 2.4643(12)
Ni-Br2	2.4139(18)	Ni1-Br2 Ni2-Br4	2.4136(10) 2.4266(8)	Ni-Br2 2.4273(13)
C6-C7	1.452(8)	C6-C7 C27-C28	1.469(6) 1.454(6)	C6-C7 1.474(8)
C7-N8	1.265(8)	C7-N8 C28-N29	1.267(5) 1.270(5)	C7-N8 1.280(7)
N8-C9	1.446(8)	N8-C9 N29-C30	1.461(5) 1.460(5)	N8-C9 1.455(7)
				1.490(6)
				1.277(5)
				1.455(5)

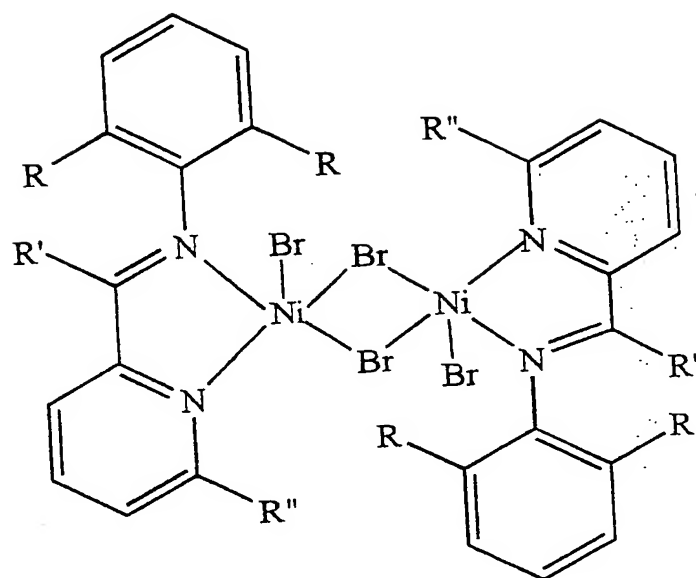
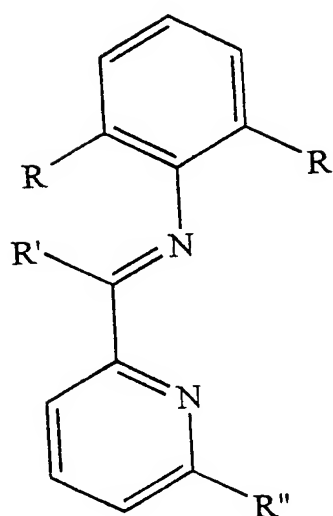
Table 5 Cont.

3	4	5	6
Bond angles			
N1-Ni-N8	N1-Ni1-N8 N22-Ni2-N29	N1-Ni-N8	N1-Ni-N8
79.4(2)	80.29(13) 80.55(13)		79.61(19)
N1-Ni-Br1	N1-Ni1-Br1 N22-Ni2-Br3	N1-Ni-Br1	N1-Ni-Br1
91.05(16)	175.99(9) 176.09(10)		84.02(14)
N1-Ni-Br1a [#]	N1-Ni1-Br1a [*] N22-Ni2-Br3a [§]	N1-Ni-Br1a [°]	N1-Ni-Br1a [†]
173.09(16)	91.58(10) 90.74(10)		169.29(14)
N1-Ni-Br2	N1-Ni1-Br2 N22-Ni2-Br4	N1-Ni-Br2	N1-Ni-Br2
91.61(16)	92.17(9) 90.97(10)		92.66(13)
N8-Ni-Br1	N8-Ni1-Br1 N29-Ni2-Br3	N8-Ni-Br1	N8-Ni-Br1
110.48(16)	99.32(10) 99.75(10)		114.91(12)
N8-Ni-Br1a [#]	N8-Ni1-Br1a [*] N29-Ni2-Br3a [§]	N8-Ni-Br1a [°]	N8-Ni-Br1a [†]
95.30(14)	107.95(10) 106.33(9)		103.25(13)
N8-Ni-Br2	N8-Ni1-Br2 N29-Ni2-Br4	N8-Ni-Br2	N8-Ni-Br2
117.05(16)	108.95(10) 107.94(9)		108.57(12)
Br1-Ni-Br1a [#]	Br1-Ni1-Br1a [*] Br3-Ni2-Br3a [§]	Br1-Ni-Br1a [°]	Br1-Ni-Br1a [†]
86.63(4)	84.73(3) 85.43(3)		85.44(3)
Br1-Ni-Br2	Br1-Ni1-Br2 Br3-Ni2-Br4	Br1-Ni-Br2	Br1-Ni-Br2
132.06(6)	91.73(4) 92.64(2)		134.89(4)
Br1a [#] -Ni-Br2	Br1a [*] -Ni1-Br2 Br3a [§] -Ni2-Br4	Br1a [°] -Ni1-Br2	Br1a [†] -Ni1-Br2
94.78(4)	143.02(3) 145.49(3)		96.12(3)
Ni-Br1-Nia [#]	Ni1-Br1-Ni1a [*] Ni2-Br3-Ni2a [§]	Ni-Br1-Nia [°]	Ni-Br1-Nia [†]
93.37(4)	95.27(3) 94.57(3)		94.56(3)

Symmetry transformations used to generate equivalent atoms: [#] -x, -y, -z+1; ^{*} -x+2, -y+1, -z+1, [§] -x+1, -y+1, -z; [°] -x+1, -y, -z+1;

[†] -x+1, -y+1, -z+1

Scheme 1



L₂: R = Me; R' = R'' = H

L₃: R = *i*Pr; R' = H; R'' = Me

L₄: R = *i*Pr; R' = Me; R'' = H

L₅: R = *i*Pr; R' = Ph; R'' = H

3: R = Me; R' = R'' = H

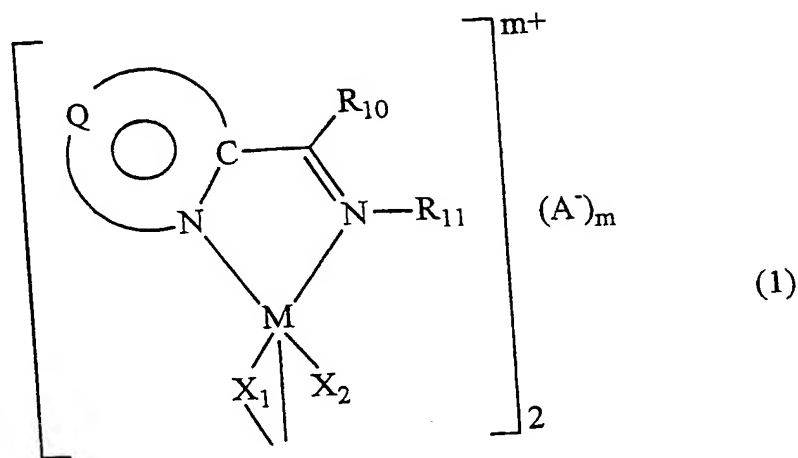
4: R = *i*Pr; R' = H; R'' = Me

5: R = *i*Pr; R' = Me; R'' = H

6: R = *i*Pr; R' = Ph; R'' = H

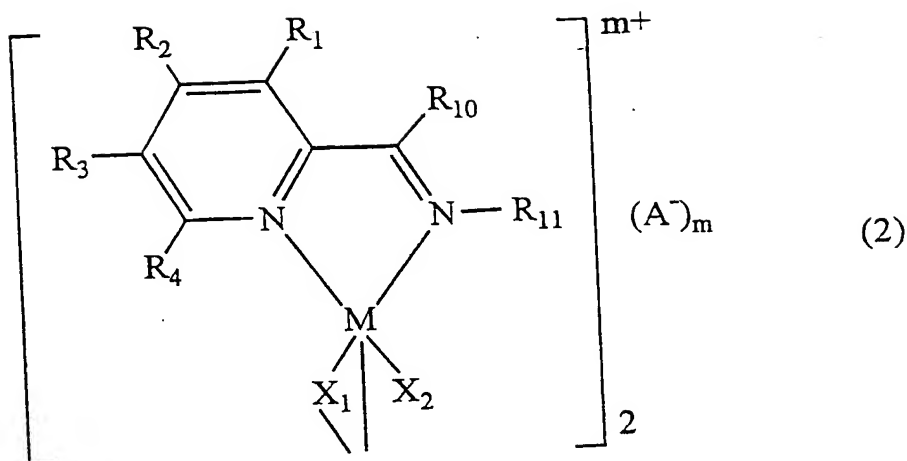
Claims

1. A dimeric late transition metal complex having the formula (1)



- wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-(\text{CR})_n\text{Z}_r-$ wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a heteroatom, and a $\text{C}_1\text{-C}_{30}$ hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from $-\text{N}=$, $-\text{NR}'-$, R' being hydrogen or a $\text{C}_1\text{-C}_{10}$ hydrocarbyl, $-\text{S}-$ and $-\text{O}-$, n is 2 or 3 and r is 0 or 1 when $n+r$ is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when $n+r$ is 4; R_{10} is hydrogen, a halogen or a $\text{C}_1\text{-C}_{30}$ hydrocarbyl; R_{11} is hydrogen, a halogen or a $\text{C}_1\text{-C}_{30}$ hydrocarbyl; M is cobalt or nickel; X_1 and X_2 are independently selected from a monovalent ligand attached to M; A^- is an anion and m is 0, 1 or 2, one of X_1 and X_2 optionally missing in the case m is 1 or 2, and the open lines from M and X_1 are M-X_1 and $\text{X}_1\text{-M}$ bonds, respectively, between the two mers of the dimer.

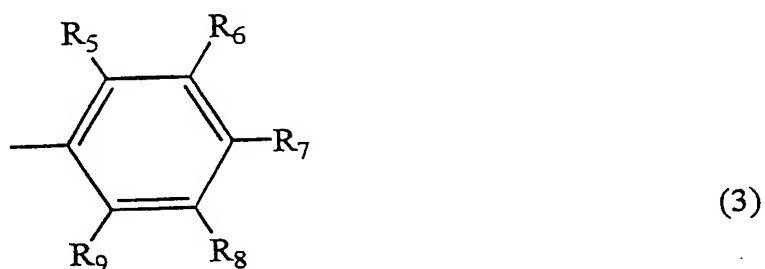
2. A dimeric late transition metal complex according to claim 1, characterized in that it comprises a bidentate N-(2-pyridinylmethylene)arylamino ligand, and has the formula (2)



wherein each of R_1 - R_4 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R_{10} is a group selected from hydrogen and a hydrocarbyl containing from 1 to 10 carbon atoms, R_{11} is an aromatic group and M , X_1 , X_2 , A^- and m are the same as above.

3. A late transition metal complex according to claim 2, characterized in that R_1 - R_4 are a hydrogen.

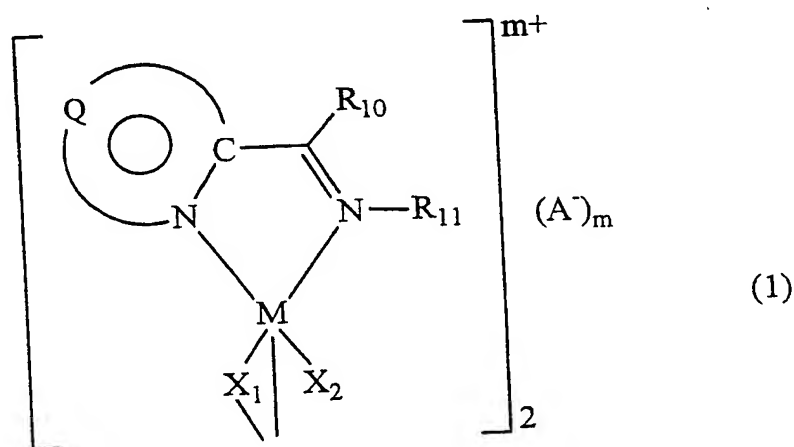
4. A late transition metal complex according to claim 2 or 3, characterized in that R_{11} has the formula (3)



wherein each of R_5 - R_9 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group.

5. A late transition metal complex according to claim 4, characterized in that R_6 - R_8 are a hydrogen and R_5 and R_9 are independently selected from a C_1 - C_{20} alkyl, a C_6 - C_{24} aryl, a C_7 - C_{30} alkaryl or a C_7 - C_{30} aralkyl.

6. A late transition metal complex according to claim 5, characterized in that R_{10} is a hydrogen and R_5 and R_9 are independently a branched C_3 - C_{10} alkyl, preferably isopropyl or tert. butyl.
7. A late transition metal complex according to claim 6, characterized in that R_5 and R_9 are isopropyl.
8. A late transition metal complex according to one of claims 1 to 7, characterized in that X_1 and X_2 are independently a hydrogen, a halogen, a C_1 - C_{12} hydrocarbyl, a C_1 - C_{12} hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound.
9. A late transition metal complex according to claim 8, characterized in that X_1 and X_2 are independently a halogen, preferably chlorine or bromine.
10. A late transition metal complex according to any of claims 1 to 9, characterized in that m is 0.
11. A late transition metal complex according to any of claims 1 to 10, characterized in that it is selected from di- μ -chlorodichlorobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II) and di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II).
12. A late transition metal catalyst system for the polymerization of ethylenically unsaturated compounds, characterized in that it comprises a dimeric late transition metal complex having the formula (1)

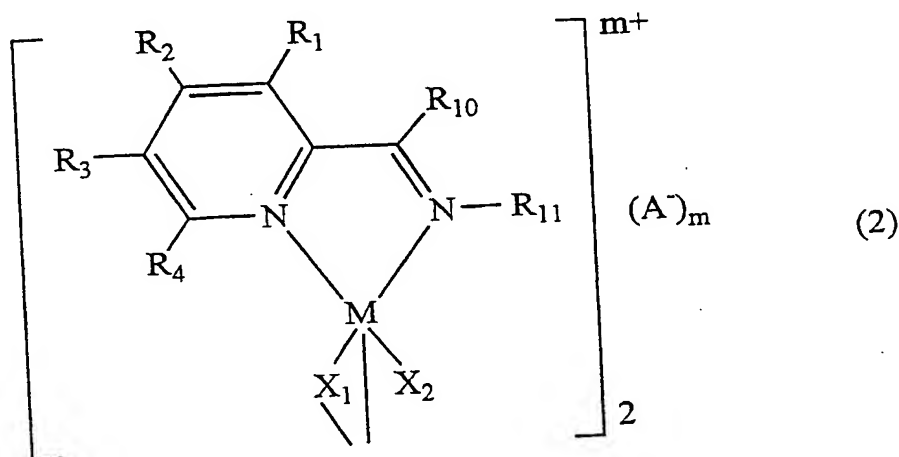


wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-(CR)_nZ-$ wherein each R is

independently selected from hydrogen, a halogen, a substituent comprising a hetero-atom, and a C₁-C₃₀ hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from -N=, -NR'-, R' being hydrogen or a C₁-C₁₀ hydrocarbyl, -S- and -O-, n is 2 or 3 and r is 0 or 1 when n+r is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when n+r is 4; R₁₀ is hydrogen, a halogen or a C₁-C₃₀ hydrocarbyl; R₁₁ is hydrogen, a halogen or a C₁-C₃₀ hydrocarbyl; M is cobalt or nickel; X₁ and X₂ are independently selected from a monovalent ligand attached to M; A⁻ is an anion and m is 0, 1 or 2, one of X₁ and X₂ optionally missing in the case m is 1 or 2, and the open lines from M and X₁ are M-X₁ and X₁-M bonds, respectively, between the two mers of the dimer.

13. A late transition metal catalyst system according to claim 12, characterized in that it comprises

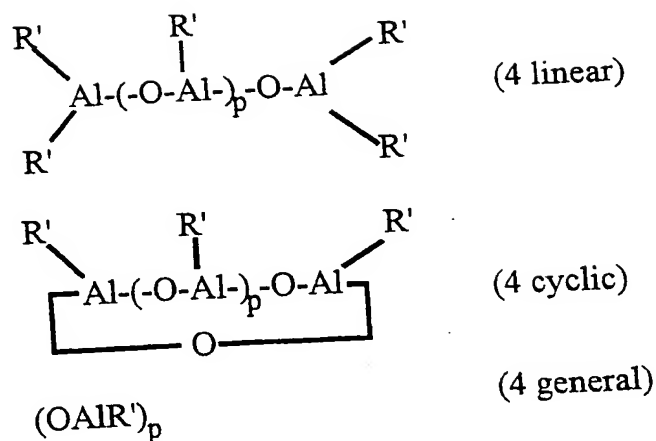
a) a dimeric late transition metal complex component having the formula (2)



15 wherein each of R₁-R₄ is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R₁₀ is a group selected from hydrogen and a hydrocarbyl containing from 1 to 10 carbon atoms, R₁₁ is an aromatic group and M, X₁, X₂ A⁻ and m are the same as above, and

20 b) a cocatalyst component selected from

(i) an aluminoxane having one of the following formulas (4)



wherein each R' is the same or different and is a C₁-C₁₀ alkyl group and p is an integer between 1 and 40, and

(ii) an organometallic compound having the formula (5)

5

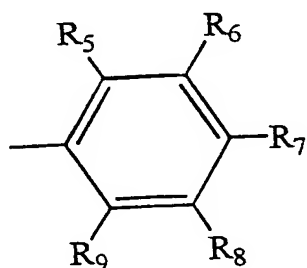


(5)

wherein R'' is a C₁-C₁₀ hydrocarbyl, X' is a halogen, q is 1, 2 or 3, r is the valency of M, M is a metal selected from Groups 1 to 3 and 13 of the Periodic Table of the Elements (IUPAC 1990), and s is 1 or 2.

14. A catalyst system according to claim 13, characterized in that R₁-R₄ are a hydrogen.

15. A catalyst system according to claim 13 or 14, characterized in that in formula (2), said R₁₁ has the formula (3)

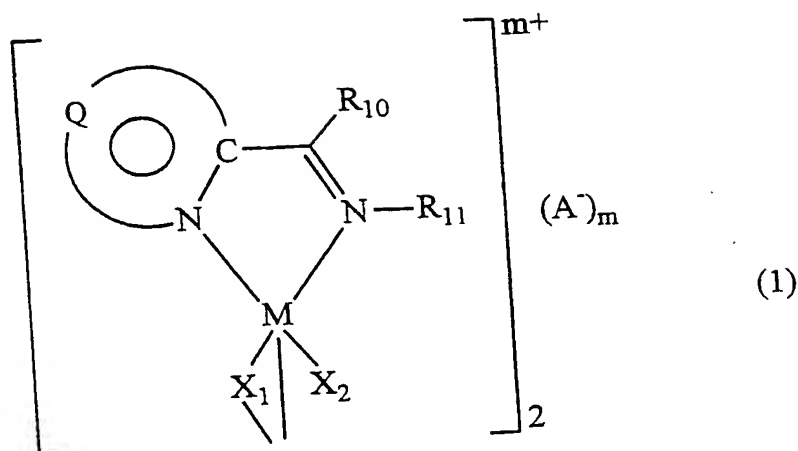


(3)

wherein each of R₅-R₉ is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group.

15

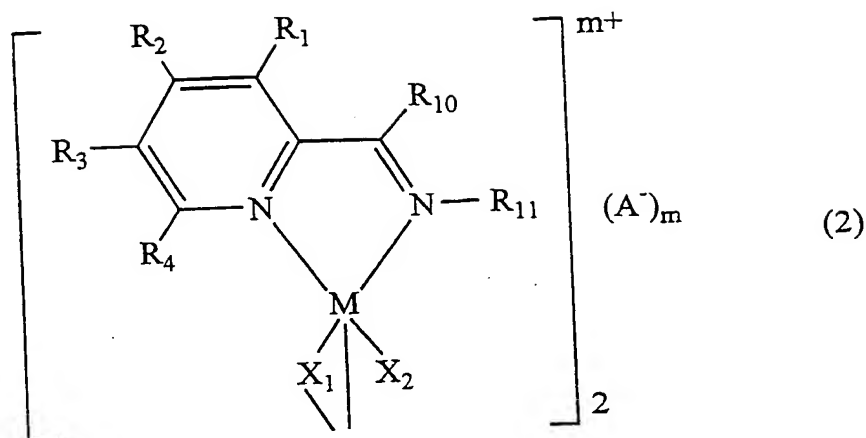
16. A catalyst system according to claim 15, characterized in that R_6 - R_8 are a hydrogen, R_5 and R_9 are independently selected from a C_1 - C_{20} alkyl, a C_6 - C_{24} aryl, a C_7 - C_{30} alkaryl or a C_7 - C_{30} aralkyl.
17. A catalyst system according to claim 16, characterized in that R_{10} is a hydrogen and R_5 and R_9 are independently a branched C_3 - C_{10} alkyl, preferably isopropyl or tert. butyl.
18. A catalyst system according to claim 17, characterized in that R_5 and R_9 are isopropyl.
19. A catalyst system according to one of claims 12 to 18, characterized in that X_1 and X_2 are independently a hydrogen, a halogen, a C_1 - C_{12} hydrocarbonyl, a C_1 - C_{12} hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound.
20. A catalyst system according to claim 19, characterized in that X_1 and X_2 are independently a halogen, preferably chlorine or bromine.
21. A catalyst system according to any of claims 12 to 20, characterized in that m is 0.
22. A catalyst system according to claim 21, characterized in that said dimeric late transition metal complex component is selected from di- μ -chlorodichlorobis-[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II) and di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]-dinickel(II).
23. A catalyst system according to any of claims 12 to 22, characterized in that said cocatalyst component is a C_1 - C_{10} aluminoxane, preferably methyl aluminoxane.
24. A catalyst system according to any of claims 13-23, characterized in that the molar ratio Al/M is between 10 and 10000, preferably between 500 and 5000.
25. A process for the polymerization of ethylenically unsaturated compounds, characterized in that at least one ethylenically unsaturated compound is under polymerization conditions contacted with a catalyst system comprising a dimeric late transition metal complex having the formula (1)



wherein: Q, C and N form an unsaturated ring of aromatic nature; the divalent group Q is a chain of 3 or 4 atoms having the formula $-[(CR)_nZ_r]-$ wherein each R is independently selected from hydrogen, a halogen, a substituent comprising a hetero-atom, and a C_1-C_{30} hydrocarbyl, Z or each Z independently occurs at any place of the chain Q and is selected from $-N=$, $-NR'-$, R' being hydrogen or a C_1-C_{10} hydrocarbyl, $-S-$ and $-O-$, n is 2 or 3 and r is 0 or 1 when $n+r$ is 3, and, n is 2, 3 or 4 and r is 0, 1 or 2 when $n+r$ is 4; R_{10} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; R_{11} is hydrogen, a halogen or a C_1-C_{30} hydrocarbyl; M is cobalt or nickel; X_1 and X_2 are independently selected from a monovalent ligand attached to M; A^- is an anion and m is 0, 1 or 2, one of X_1 and X_2 optionally missing in the case m is 1 or 2, and the open lines from M and X_1 are $M-X_1$ and X_1-M bonds, respectively, between the two mers of the dimer.

26. Process according to claim 25, characterized in that, under polymerization conditions, at least one polymerizable ethylenically unsaturated compound is contacted with a catalyst system comprising

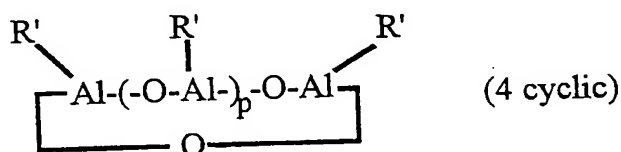
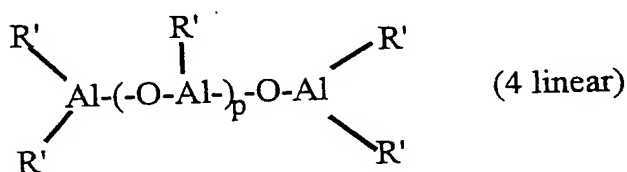
a) a dimeric late transition metal complex component having the formula (2)



wherein each of R_1 - R_4 is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group, R_{10} is a group selected from hydrogen and a hydrocarbyl containing from 1 to 10 carbon atoms, R_{11} is an aromatic group and M , X_1 , X_2 , A^- and m are the same as above, and

b) a cocatalyst component selected from

(i) an aluminoxane having one of the following formulas (4)



wherein each R' is the same or different and is a C_1 - C_{10} alkyl group and p is an integer, between 1 and 40, and

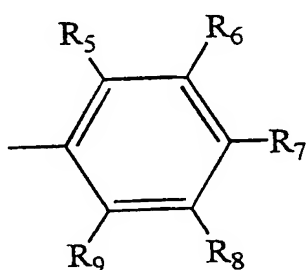
(ii) an organometallic compound having the formula (5)



wherein R" is a C₁-C₁₀ hydrocarbyl, X' is a halogen, q is 1, 2 or 3, r is the valency of M, M is a metal selected from Groups 1 to 3 and 13 of the Periodic Table of the Elements (IUPAC 1990), and s is 1 or 2.

27. A polymerization process according to claim 26, characterized in that in
5 formula (6), R₁-R₄ are a hydrogen.

28. A polymerization process according to claim 26 or 27, characterized in that in
formula (2), said R₁₁ has the formula (3)



(3)

10 wherein each of R₅-R₉ is a substituent independently selected from a hydrogen, an organic group or ring constituent containing from 1 to 20 carbon atoms, or an inorganic atom or group.

29. A polymerization process according to claim 28, characterized in that R₆-R₈ are a hydrogen and R₅ and R₉ are independently a C₁-C₂₀ alkyl, a C₆-C₂₄ aryl, a C₇-C₃₀ alkaryl or a C₇-C₃₀ aralkyl.

15 30. A polymerization process according to claim 29, characterized in that R₁₀ is a hydrogen and R₅ and R₉ are independently a branched C₃-C₁₀ alkyl, preferably isopropyl or tert. butyl.

31. A polymerization process according to claim 30, characterized in that R₅ and R₉ are isopropyl.

20 32. A catalyst system according to one of claims 26 to 31, characterized in that in formula (6), X₁ and X₂ are independently a hydrogen, a halogen, a C₁-C₁₂ hydrocarbyl, a C₁-C₁₂ hydrocarbyloxy, and, in the case m is 1 or 2, optionally an electron donor compound.

25 33. A catalyst system according to claim 32, characterized in that X₁ and X₂ are independently a halogen, preferably chlorine or bromine.

34. A catalyst system according to any of claims 26 to 33, **characterized** in that in formula (2), m is 0.

35. A polymerization process according to claim 34, **characterized** in that said late transition metal complex component is selected from di- μ -chlorodichlorobis-
5 [2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]dinickel(II) and di- μ -bromodibromobis[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine]-dinickel(II).

36. A polymerization process according to any of claims 26 to 35, **characterized** in that said cocatalyst component is a C_1 - C_{10} aluminoxane, preferably methyl
10 aluminoxane.

37. A polymerization process according to claim 36, **characterized** in that in said polymerization catalyst system, the molar ratio Al/M is between 10 and 10 000, preferably between 500 and 5000.

38. A polymerization process according to any of claims 25 to 37, **characterized** in that said ethylenically unsaturated compound is selected from ethylene, an
15 α - C_3 - C_{20} olefin, a conjugated C_4 - C_{12} diene and an α - ω - C_5 - C_{14} diolefin and polymerizable combinations thereof.

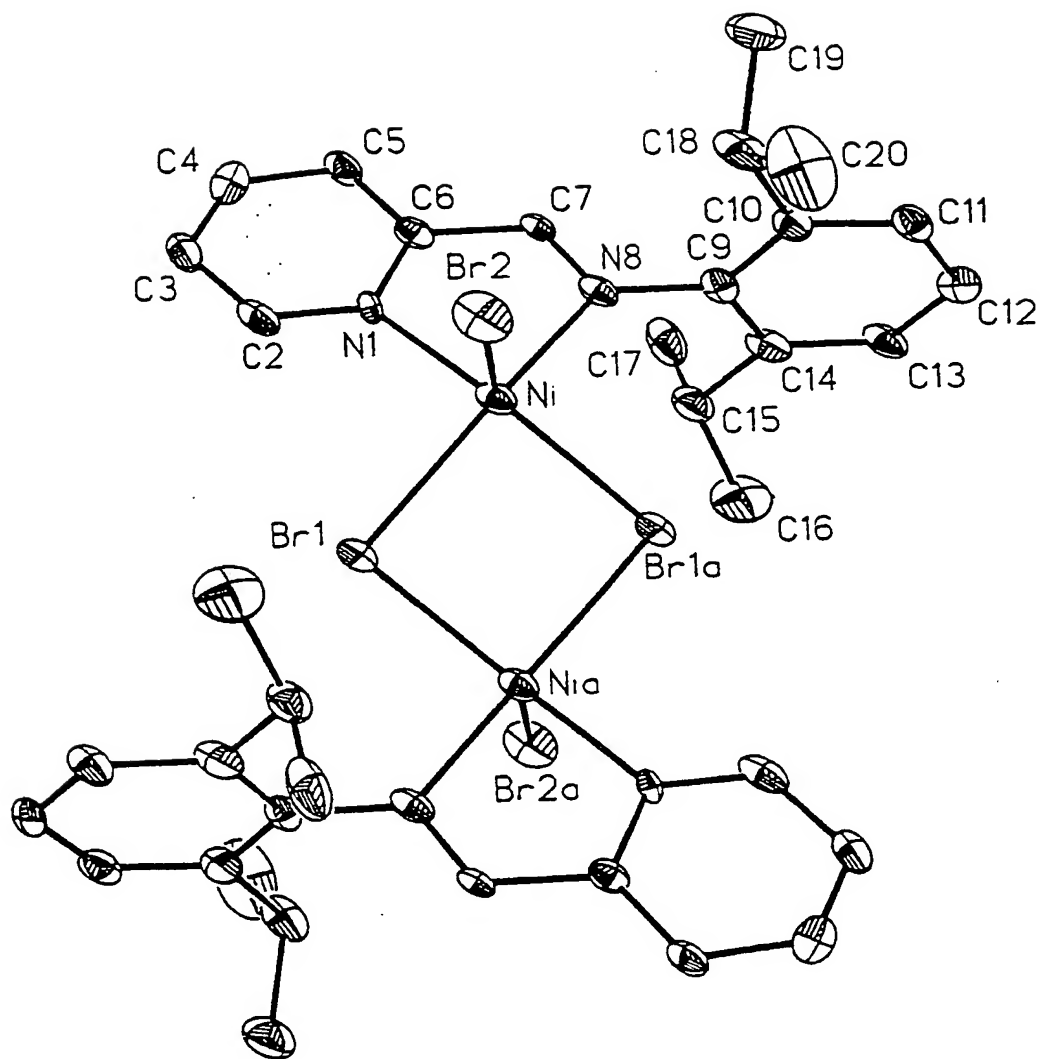


Fig. 1

Fig. 2

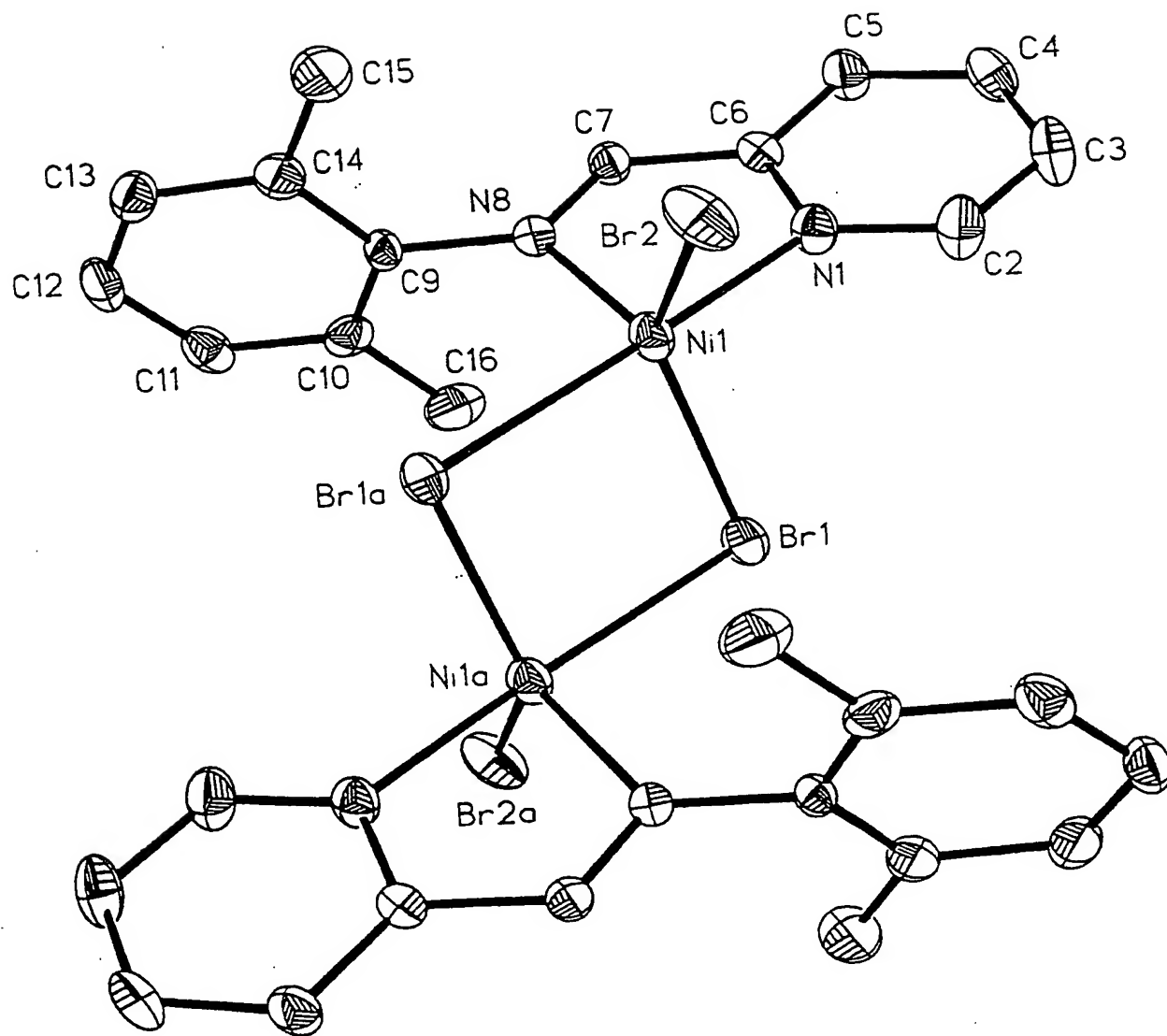


Fig. 3

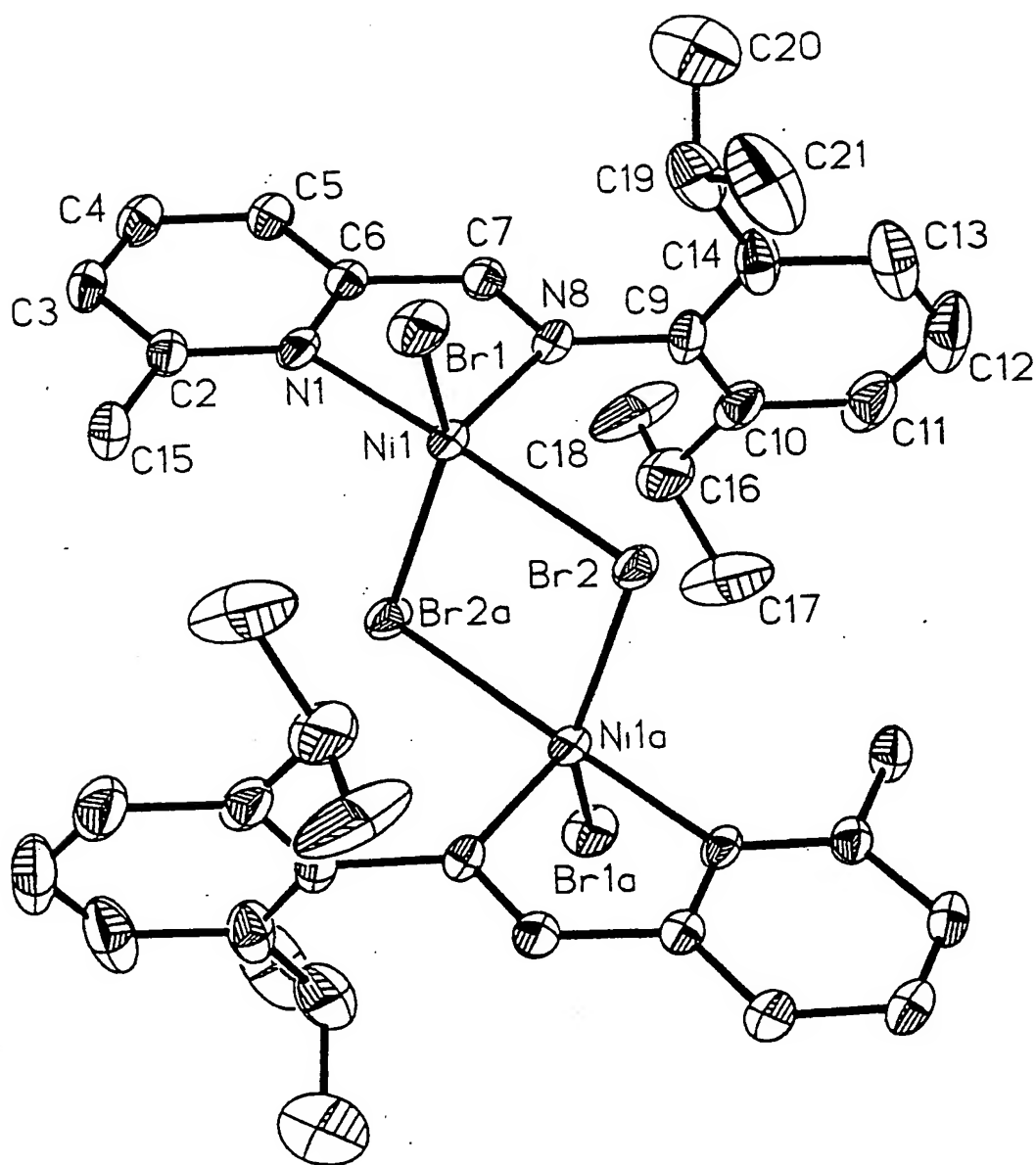


Fig. 4a

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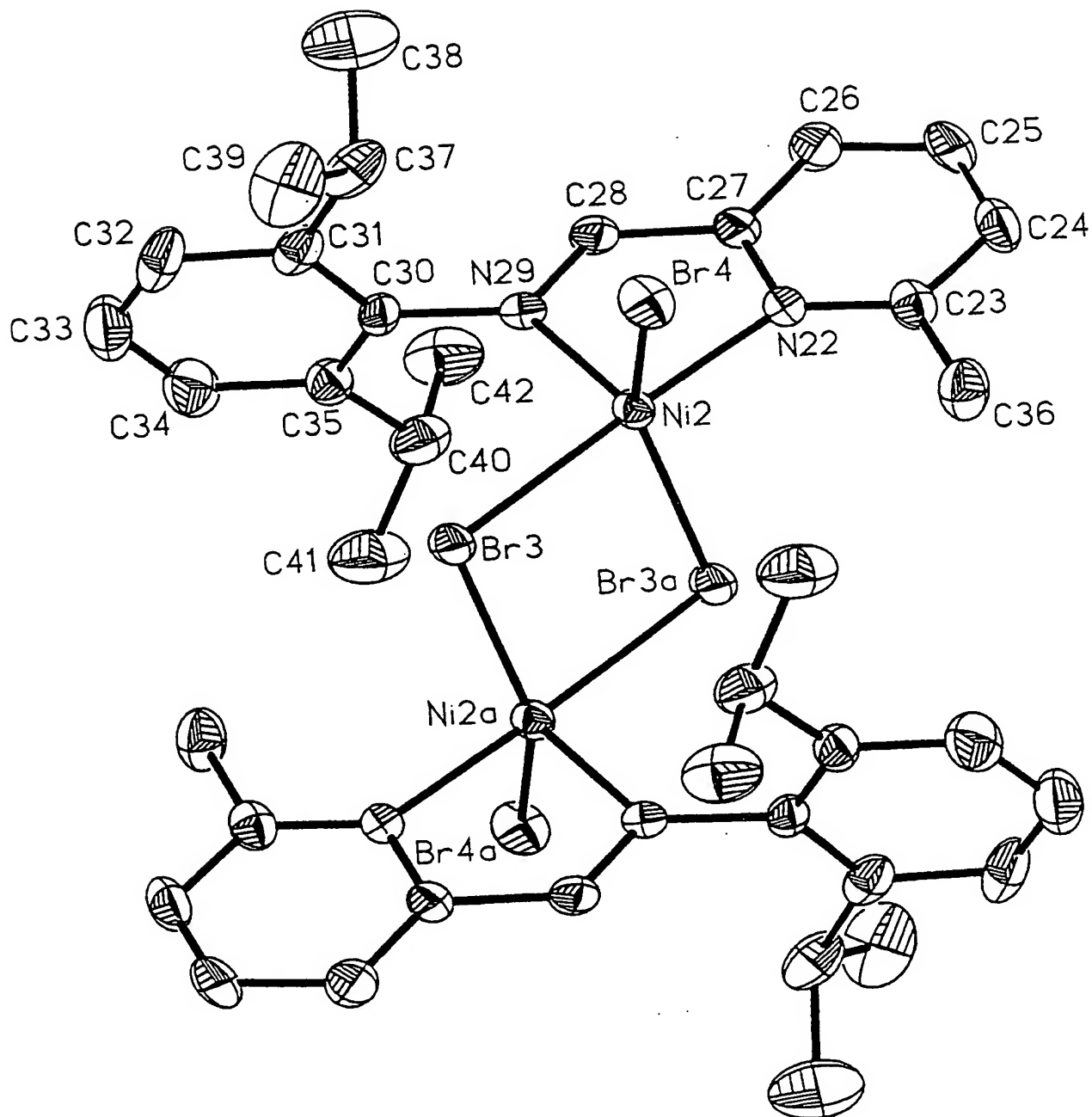


Fig. 4b

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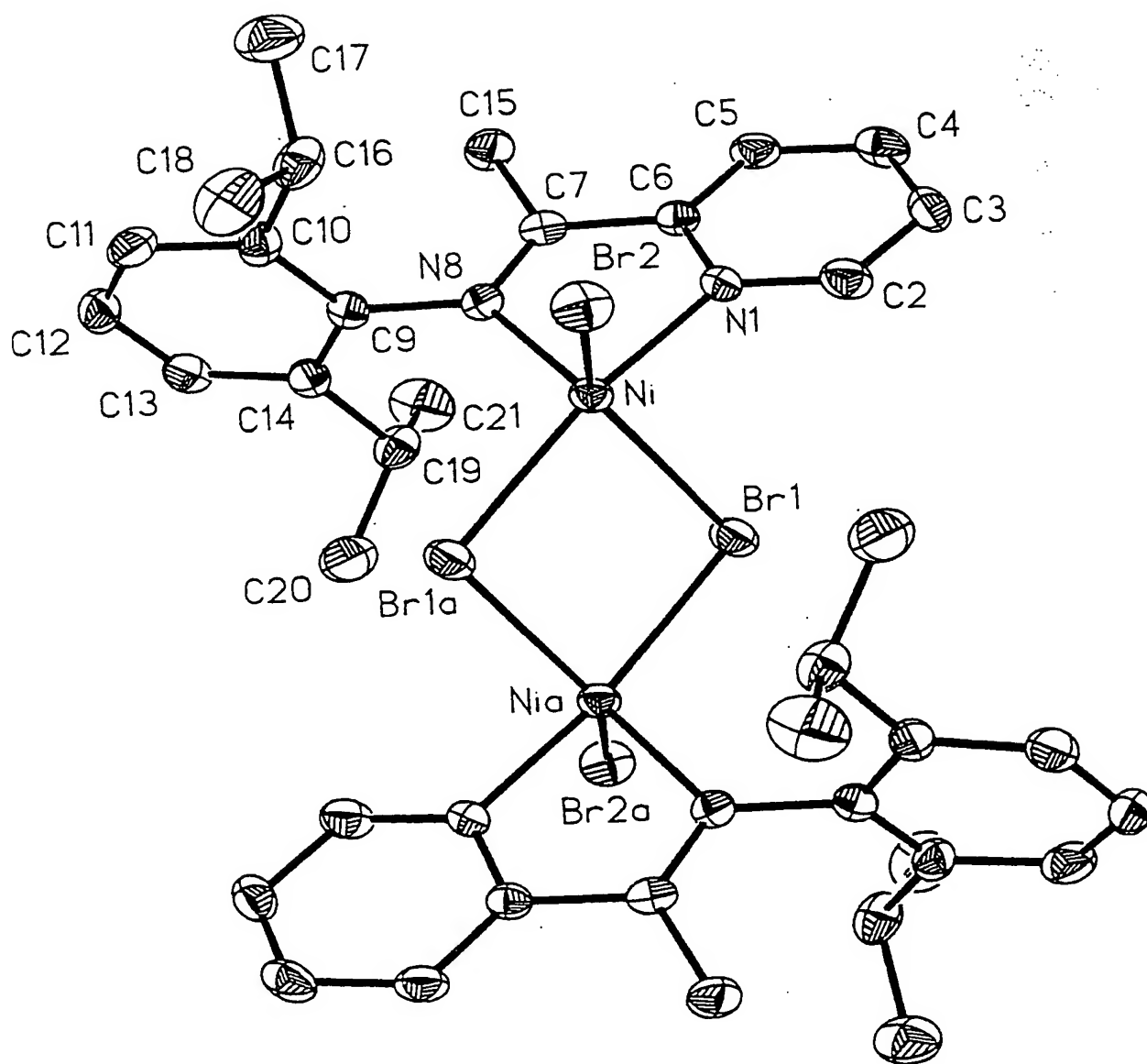


Fig. 5

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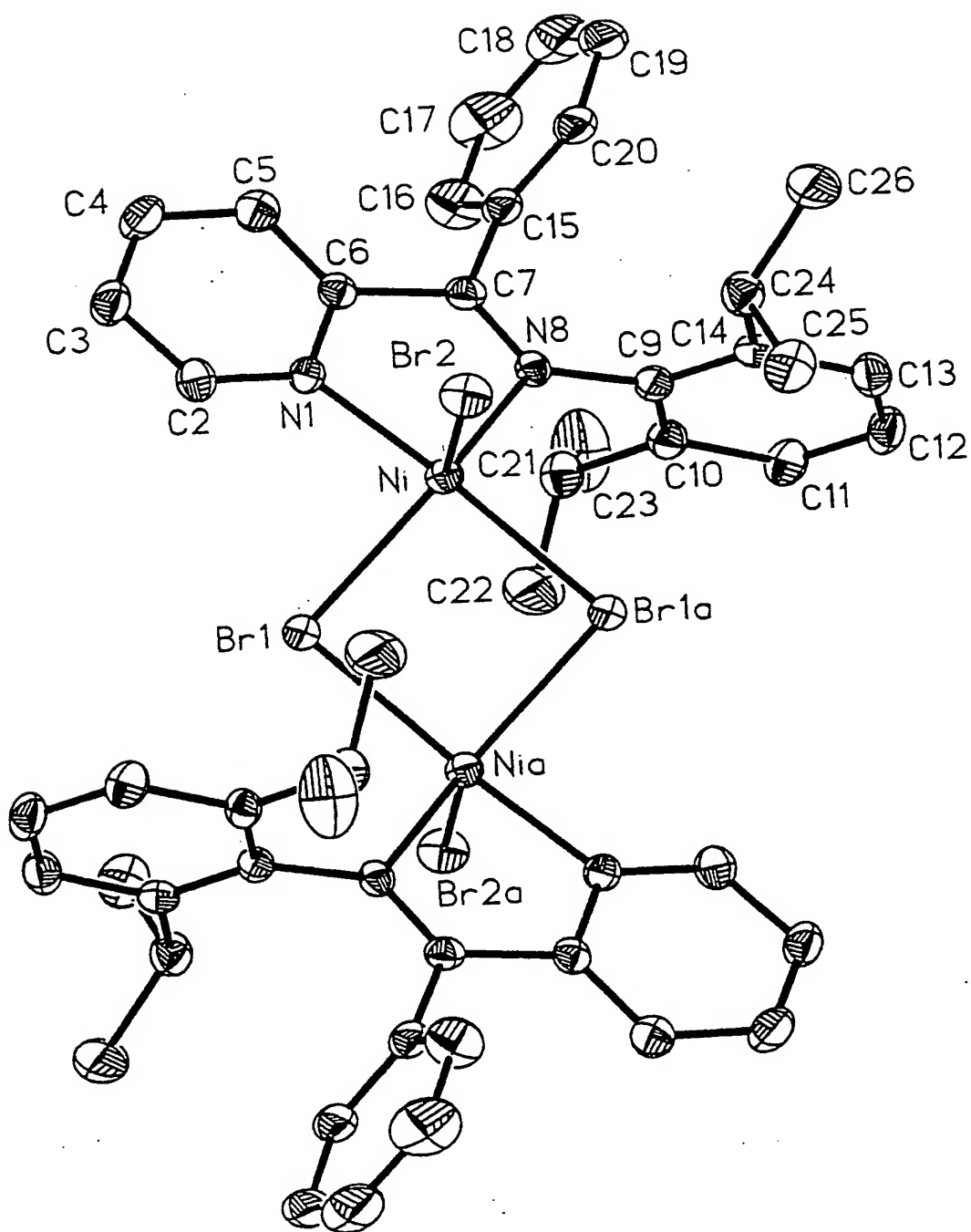


Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI 99/00803

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F15/02 C07F15/04 C07F15/06 C07F15/00 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LAINE, T.V. ET AL.: "synthesis and x-ray structures of new mononuclear and dinuclear diimine complexes of late transition metal complexes" EUROPEAN JOURNAL OF INORGANIC CHEMISTRY, no. 6, 1999, pages 959-964, XP002126973 the whole document	1-38
X	CHEMICAL ABSTRACTS, vol. 131, Columbus, Ohio, US; abstract no. 299740, LAINE, T.V. ET AL.: "polymerization of ethylene with new diimine complexes of late transition metals" XP002126974 abstract & MACROMOL. RAPID COMMUN., vol. 20, no. 9, 1999, pages 487-491,	1-38

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

6 January 2000

Date of mailing of the international search report

20/01/2000

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